PB81-122996

Comparison of Gas Phase Hydrocarbon Emissions from Light-Duty Gasoline Vehicles and Light-Duty Vehicles Equipped with Diesel Engines

(U.S.) Environmental Protection Agency
Ann Arbor, MI

Sep 80

U.S. Department of Commerce
National Technical Information Service
NTIS.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECI PB81-122996
EPA-AA-CTAB/PA/80-5		

4. TITLE AND SUBTITLE	5. REPORT DATE
Comparison of Gas Phase Hydrocarbon Emissions from Light-Duty Gasoline Vehicles and Light-Duty Vehicles Equipped with Diesel Engines	September 1980 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Penny Carey and Janet Cohen	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS U.S. Environmental Protection Agency Office of Mobile Source Air Pollution Control Emission Control Technology Division Ann Arbor, Michigan 48105	10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Box 9	13. TYPE OF REPORT AND PERIOD COVERED Technical 14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

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16. ABSTRACT

The purpose of this document is to consolidate much of the existing data on gas phase hydrocarbon exhaust emissions from both gasoline vehicles and vehicles equipped with diesel engines. This subject is of interest because new studies have shown diesel emissions to contain compounds of high molecular weight. This high molecular weight component is dominated by particle-bound hydrocarbons; however, the potential health risk associated with heavy hydrocarbons merits examination of the gas phase as well. Particular emphasis will be placed on the comparison of emissions and their potential carcinogenicity. Other areas to be discussed include evaporative hydrocarbon emissions and the effect of fuel composition on gasoline gaseous hydrocarbon emissions.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Hydrocarbons ~~Carcinogenics~~ Carcinogens Automobiles Motor vehicles Exhaust gases Exhaust emissions Diesel engines Gasoline engines	Carcinogenicity	

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
Release unlimited	Unclassified	
	20. SECURITY CLASS (This page) Unclassified	22. PRICE

EPA Form 2220-1 (9-73)

REPRODUCED BY
NATIONAL TECHNICAL INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

EPA-AA-CTAB/PA/80-5

TECHNICAL REPORT

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by

Penny Carey
Janet Cohen

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Control Technology Assessment and Characterization Branch
Emission Control Technology Division
Office of Mobile Source Air Pollution Control
Office of Air, Noise and Radiation
U.S. Environmental Protection Agency
2565 Plymouth Road
Ann Arbor, Michigan 48105

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I. Introduction

The composition of the hydrocarbons in automobile exhaust is profoundly influenced by many factors, including emission control systems. The use of catalytic converter control systems, for example, has brought about a significant change in the detailed patterns of the hydrocarbon emissions from gasoline vehicles. The composition of the hydrocarbon mixture in gasoline catalyst and non-catalyst automobile exhaust gases has been extensively studied and individual hydrocarbon data is available. This type of detailed information is not available for Diesel emissions at this time because Diesel emissions contain hydrocarbons of higher molecular weight than gasoline emissions. The gas chromatograph systems used to date do not have adequate resolution to permit identification of many of these higher molecular weight hydrocarbons; therefore, the available hydrocarbon data for Diesel equipped vehicles is mostly in terms of carbon number. Currently, particle-bound organic emissions from vehicles equipped with Diesel engines are being studied; however, not only particle-bound organics are emitted in Diesel exhaust. A significant fraction of the total organics are emitted in the gas phase.

Hydrocarbons are regulated by the EPA because of their participation in atmospheric photochemistry, creating ozone. Regulation of hydrocarbon emissions, historically, has been based on potential atmospheric photochemistry rather than potential carcinogenicity. Individual hydrocarbon carcinogenic potency may be an important factor to consider in future regulations.

Few comparisons of Diesel and gasoline gaseous hydrocarbon emissions have been made to date. The purpose of this document is to consolidate much of the existing data on gas phase hydrocarbon exhaust emissions from both gasoline vehicles and vehicles equipped with Diesel engines. This subject is of interest because new studies have shown Diesel emissions to contain compounds of high molecular weight. This high molecular weight component is dominated by particle-bound hydrocarbons; however, the potential health risk associated with heavy hydrocarbons merits examination of the gas phase as well. Particular emphasis will be placed on the comparison of emissions and their potential carcinogenicity. Other areas to be discussed include evaporative hydrocarbon emissions and the effect of fuel composition on gasoline gaseous hydrocarbon emissions.

II. Gasoline Vehicles

A. Tailpipe Emissions

The hydrocarbon composition of gasoline engine exhaust consists primarily of components with carbon numbers 1 through 10. These hydrocarbons exhibit distinct peaks on a gas chromatograph profile. The individual compounds, therefore, can be readily identified. Table 1 lists the individual hydrocarbons corresponding to the

NR = NONREACTIVE
O = OLEFIN
P = PARAFFIN
A = AROMATIC

TABLE 1

INDIVIDUAL HYDROCARBONS IN GASOLINE ENGINE EXHAUST

Peak No.	Compound	Class	Carbon Number
1	Methane	NR	1
2	Ethylene	O	2
3	Ethane	NR	2
4	Acetylene	NR	2
5	Propylene; propane	O	3
6	Propadiene	O	3
7	Methyl acetylene	O	3
8	Isobutane	P	4
9	Butene 1; isobutylene	O	4
10	N-butane; 1, 3-butadiene	.8P/.20	4
11	Trans-2-butene	O	4
12	Cis-2-butene	O	4
13	3-methyl-1-butene	O	5
14	Isopentane	P	5
15	Pentene-1	O	5
16	N-pentane; 2-methyl-1-butene	.9P/.10	5
17	Trans-2-pentene	O	5
18	Cis-2-pentene	O	5
19	2-methyl-2-butene	O	5
20	Cyclopentane; 3-methyl-1-pentene	P	5/6
21	2,3-dimethylbutane	P	6
22	2-methylpentane; 2,3-dimeth-1-butene	.94P/.060	6
23	3-methylpentane	P	6
24	1-hexene; 2-ethyl-1-butene	O	6
25	N-hexane; cis-3-hexene	P	6
26	2 methyl-2-pentene	O	6
27	Methylcyclopentane; 3-methtrans-2-pentene	.93P/.070	6
28	2,4-dimethylpentane	P	7
29	Methylcyclopentene	O	6
30	Benzene, cyclohexane	.5P/.5NR	6
31	Cyclohexene; 2,3-dimethylpentane; 2-methylhexane	.92P/.080	6/7/7
32	3-methylhexane	P	7
33	Isooctane	P	8
34	N-heptane	P	7
35	Methylcyclohexane	P	7
36	2,4 and 2,5-dimethylhexane	P	8
37	2,3,4-trimethylpentane	P	8
38	2,3,3-trimethylpentane	P	8
39	Toluene; 2,3-dimethylhexane	.02P/.98A	7/8
40	2-methylheptane	P	8
41	3-methylheptane	P	8
42	2,2,5-trimethylhexane	P	9
43	N-octane	P	8
44	2,3,5-trimethylhexane	P	9
45	2,4-dimethylheptane	P	9
46	2,5 and 3,5-dimethylheptane	P	9
47	Ethylbenzene; 2,3-dimethylheptane	.1P/.9A	8/9
48	P-xylene; m-xylene; 4-methyloctane	.1P/.9A	8/9
49	O-xylene; unk C9 paraffin	.05P/.95A	8/9
50	Nonane	P	9
51	N-propylbenzene	A	9
52	1-methyl 3-ethyl-benzene; unk C10 paraffin	.07P/.93A	9/10
53	1-methyl 3-ethylbenzene; unk C10 paraffin	.25P/.75A	9/10
54	Mesitylene	A	9
55	1,2,4-trimethylbenzene	A	9
56	Secbutylbenzene; n-decane	.6P/.4A	10
57	Unknowns	.8P/.20	

chromatograph peaks. The class and carbon number for each compound are also listed. Some of these compounds peak, or elute, at the same time on the gas chromatograph. It should be noted that the percentage each compound contributes to a peak and the distribution of the various classes of compounds are fuel related.

All of the data for the gasoline vehicles has been taken from a paper written by F. Black and L. High of the Environmental Protection Agency facility at Research Triangle Park, North Carolina[1]. Individual hydrocarbon emission rates were determined for 22 motor vehicles, 18 of which will be presented here. The vehicle types and the corresponding number tested are listed below.

Vehicle Type	Number
Not catalyst-equipped	1
Catalyst-equipped	13
"lean-burn" without catalyst	4
Total	18

In this paper, emphasis is placed on catalyst, and to a lesser extent, lean-burn systems since they currently dominate the approaches to emission control. Table 2 presents the data in terms of class of compound, Table 3 in terms of carbon number, and Table 4 in terms of individual components. The 1975 Federal Test Procedure (FTP) was used in all emissions testing reported here. The samples were collected using a constant volume sampler and analyzed by gas chromatography coupled to a flame ionization detector. The gasoline used for the catalyst and lean-burn vehicles was a test fuel with a Reid Vapor Pressure of 10.2 psi and was composed of 26.2% aromatics, 6.5% olefins and 67.3% paraffins.

A comprehensive paper was published by Marvin Jackson of General Motor's Environmental Activities Staff entitled "Effect of Catalytic Emission Control on Exhaust Hydrocarbon Composition and Reactivity"[2]. Data was presented in terms of carbon percent of total hydrocarbons. Weight percents were not included and so the data is not presented here. However, Marvin Jackson did convert Frank Black's data to carbon percents so both sets of data could be compared directly. Jackson's data agrees quite well with that reported by the EPA. The few differences occur in the fuel-type hydrocarbons and, according to Jackson, are probably caused by fuel composition differences.

From Table 2 it can be seen that vehicles equipped with oxidation catalysts emit a higher percentage of methane in their exhaust than do non-catalyst or lean-burn equipped vehicles. Most catalytic converter systems preferentially oxidize non-methane hydrocarbons because methane is harder for the catalytic converter to oxidize. Methane is not a significant photochemical emission because it is essentially non-reactive. Thus, the total photochemical reactivity of the hydrocarbon (HC) mixture tends to be reduced by the catalyst. In addition, the catalyst reduces the total hydrocarbon mass and generally oxidizes the unsaturated HC compounds to a greater extent than the saturated compounds.

TABLE 2

VEHICLE	CONTROL SYSTEM	TOTAL HC mg/mile	PERCENTAGE OF TOTAL HC, WT%				
NON-CATALYST			METHANE	PARAFFIN	ACETYLENE	AROMATIC	OLEFIN
1972 Chev. 350 CID	Eng. MOD.	1150	9.3	40.6	11.0	22.3	26.1
CATALYST							
1975 Ply. Fury 318 CID	Oxidation Catalyst	490	9.4	61.8	2.0	18.9	17.9
1975 Chev. Impala 350 CID	Oxidation Catalyst	250	15.5	57.1	2.7	19.7	20.9
1975 Ford Granada 302 CID	Ox. Catalyst Air Pump	920	4.8	68.1	0.5	14.7	16.9
1976 Ford Mustang 302 CID	Ox. Catalyst Air Pump	550	15.3	56.6	3.4	19.5	20.5
1976 Ford LTD 400 CID	Ox. Catalyst Air Pump	630	14.7	63.9	3.3	15.8	17.0
1977 Chrysler NY 400 CID	Ox. Catalyst Air Pump	260	26.2	68.0	2.5	11.8	17.7
1977 Dodge 360 CID	Ox. Catalyst Air Pump	230	29.7	67.3	2.2	15.5	15.0
1977 Ply. Fury, 318 CID	Ox. Catalyst Air Pump	330	18.8	60.9	4.4	16.9	17.8
1977 Ply. Fury, 225 CID	Ox. Catalyst Air Pump	840	14.4	58.0	3.4	18.6	20.0
1977 Chev. Nova, 305 CID	Oxidation Catalyst	620	14.9	50.7	9.5	21.4	18.4
1977 Chev. Vega 140 CID	Ox. Catalyst Pulsed Air	230	18.3	61.1	1.9	17.7	19.3
1977 VW Rabbit	Oxidation Catalyst	180	18.7	64.0	2.9	18.7	14.5
1977 Audi Fox	Oxidation Catalyst	270	14.5	55.3	1.7	22.6	20.4
AVERAGE		450	16.6	61.0	3.1	17.8	18.1
LEAN-BURN							
1976 Cordoba 440 CID	Electronic Lean-Burn	660	3.7	34.2	8.1	24.2	33.5
1976 Ply. Fury 318 CID	Elec. Lean-Burn Air Pump	1450	2.8	43.5	4.7	23.6	28.2
Chrysler Imp. Prototype 440 CID	Electronic Lean-Burn	390	4.8	29.5	11.1	19.9	35.0
Chrysler Imp. Prototype 440 CID	Electronic Lean-Burn	470	3.5	34.5	9.8	19.7	36.0
AVERAGE		740	3.7	35.4	8.4	21.9	34.1

TABLE 3

Gasoline Vehicle Hydrocarbon Emission Rates in Terms of Carbon Number

CARBON NUMBER	NON-CATALYST		CATALYST		LEAN-BURN	
	mg/mi	wt.%	mg/mi	wt.%	mg/mi	wt.%
1	107	9.3	64	14.3	25	3.4
2	289	25.1	54	12.0	165	22.3
3	78	6.8	15	3.4	57	7.7
4	101	8.7	33	7.5	63	8.5
5	94	8.2	71	15.9	76	10.2
6	97	8.4	35	7.8	64	8.6
7	166	14.4	72	16.1	128	17.2
8	136	11.8	74	16.5	107	14.4
9	38	3.3	14	3.2	28	3.8
10	4	0.3	1	0.2	1	0.2
Unknowns	42	3.7	14	3.1	28	3.7
THC	1150	100.0	450	100.0	740	100.0

TABLE 4

FTP Hydrocarbon Emission Rates, mg/mi.*

		Non-Catalyst	Catalyst	Lean-Burn
1	Methane	106.9	64.1	25.2
2	Ethylene	149.1	27.6	108.8
3	Ethane	13.3	11.5	5.0
4	Acetylene	127.0	14.4	51.4
5	Propylene; propane	70.0	15.0	55.6
6	Propadiene	trace	.2	.3
7	Methyl acetylene	trace	--	1.1
8	Isobutane	9.2	1.3	4.4
9	Butene 1; isobutylene	19.2	7.1	23.1
10	N-butane; 1, 3-butadiene	64.7	21.7	24.7
11	Trans-2-butene	2.7	1.7	6.6
12	Cis-2-butene	5.0	1.5	4.5
13	3-methyl-1-butene	3.0	.4	1.9
14	Isopentane	31.2	23.3	24.0
15	Pentene-1	.8	.3	1.1
16	N-pentane; 2-methyl-1-butene	24.9	18.5	17.9
17	Trans-2-pentene	1.6	.9	2.6
18	Cis-2-pentene	.7	1.2	2.8
19	2-methyl-2-butene	10.3	12.7	10.7
20	Cyclopentane;3-methyl-1-pentene	43.6	27.0	29.2
21	2,3-dimethylbutane	4.4	2.3	2.5
22	2-methylpentane; 2,3-dimeth-1-butene	4.1	2.4	5.0
23	3-methylpentane	1.5	1.3	2.3
24	1-hexene;2-ethyl-1-butene	.7	.4	1.9
25	N-hexane; cis-3-hexene	1.4	1.2	3.9
26	2 methyl-2-pentene	1.3	.8	2.8
27	Methylcyclopentane; 3-methtrans-2-pentene	1.6	.9	2.6
28	2,4-dimethylpentane	1.8	1.3	2.0
29	Methylcyclopentene	2.8	.7	.6
30	Benzene, cyclohexane	57.0	10.1	26.5
31	Cyclohexene; 2,3-dimethylpentane; 2-methylhexane	9.2	15.3	18.6
32	3-methylhexane	trace	3.4	5.8
33	Isooctane	47.0	30.5	34.2
34	N-heptane	5.5	4.2	4.4
35	Methylcyclohexance	2.2	2.0	3.6
36	2,4 and 2,5-dimethylhexane	6.7	4.6	5.9
37	2,3,4-trimethylpentane	2.9	4.2	5.6
38	2,3,3-trimethylpentane	2.5	.9	--
39	Toluene; 2,3-dimethylhexane	151.4	47.9	96.9
40	2-methylheptane	9.6	6.0	6.1
41	3-methylheptane	6.7	4.9	7.0
42	2,2,5-trimethylhexane	1.4	1.3	1.6
43	N-octane	3.7	3.4	3.8
44	2,3,5-trimethylhexane	.1	.1	.1
45	2,4-dimethylheptane	.8	.6	.7
46	2,5 and 3,5-dimethylheptane	1.6	.8	.8
47	Ethylbenzene; 2,3-dimethylheptane	10.2	3.8	7.4
48	P-xylene; m-xylene; 4-methyloctane	34.2	11.6	24.8
49	O-xylene; unk C_9 paraffin	15.1	4.7	11.6
50	Nonane	3.1	1.1	2.2
51	N-propylbenzene	1.2	.8	1.3
52	1-methyl 3-ethyl-benzene; unk C_{10} paraffin	7.4	2.6	4.9
53	1-methyl-2-ethylbenzene; unk C_{10} paraffin	5.4	.3	--
54	Mesitylene	3.6	1.7	4.0
55	1,2,4-trimethylbenzene	10.0	3.6	9.3
56	Secbutylbenzene; n-decane	2.0	.7	.8
57	Unknowns	42.0	14.0	21.1
	TOTAL	1150.	450.	740.

* BASED ON 1 NON-CATALYST, 13 CATALYST-EQUIPPED AND 4 LEAN-BURN VEHICLES

For the catalyst-equipped vehicles tested, the methane emissions ranged from about 4.8 to about 29.7% of the THC with an average of 16.6%. For the vehicles using a lean-combustion emission control system, the methane emissions ranged from about 2.8 to about 4.8% of the THC with an average of about 3.7%. It appears that lean-combustion is not as effective as oxidation catalyst control in reducing the amount of unsaturated hydrocarbons in the exhaust. The relative abundance of olefins in lean-combustion exhaust (34.3% of THC) was significantly higher than in catalyst exhaust (18.1% of THC). The aromatic level was 21.9% with lean-combustion and 17.8% with catalysts. Acetylene averaged 8.4% with lean-combustion and 3.1% with catalysts. In contrast, the paraffin level (composed of saturated hydrocarbons) averaged 61.0% for the catalysts and only 35.4% for the lean-combustion exhaust. The total hydrocarbon mass was higher for lean-combustion equipped vehicles (450 mg/mile THC for the catalyst and 740 mg/mile THC for the lean-burn system). Figure 1 graphically illustrates the data.

Table 3 presents the data in terms of carbon number. The most apparent differences in hydrocarbons emitted under the 3 control options occur at carbon numbers 1, 2 and 5. These differences can at least be partially accounted for by the ability of the catalyst to oxidize unsaturated hydrocarbons. Table 4 presents a more detailed hydrocarbon comparison. The lean-burn equipped vehicles emitted less total hydrocarbon and their exhaust hydrocarbon mixture was lower in photochemical reactivity than the non-catalyst-equipped vehicles. It is evident that the hydrocarbon composition of tailpipe emissions is sensitive to the emission control system used. The emission data presented here represents the case for vehicles run under ideal operating conditions. It should be noted that in-use vehicles may not have the same emissions due to mis-fueled or poorly maintained vehicles, different driving cycles and different temperatures.

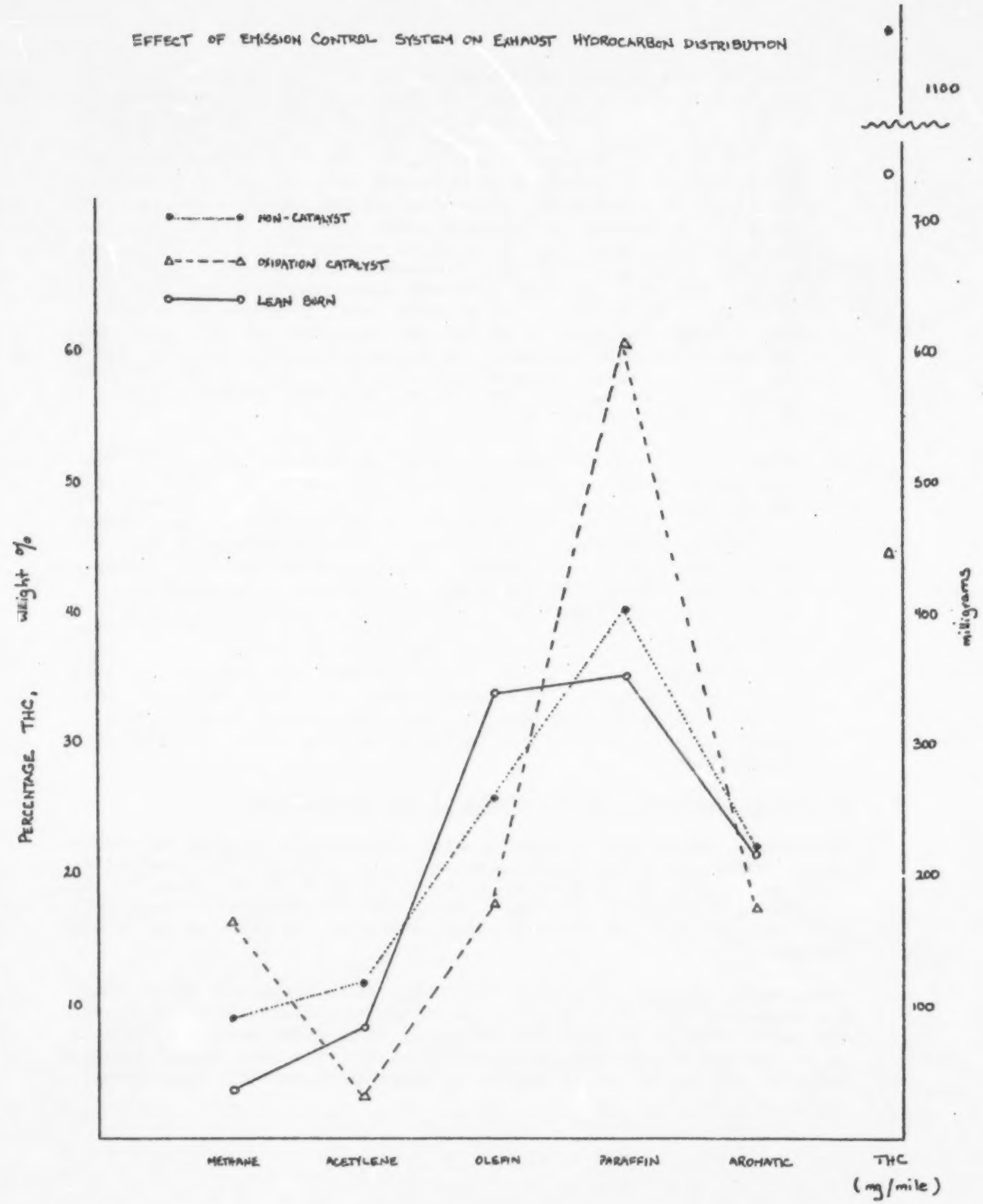
B. Evaporative Emissions and the Effect of Fuel Composition

Hydrocarbon composition is significantly different in tailpipe and evaporative emissions. The information and data used for the evaporative emission analysis was taken from another paper by F. Black, et.al.[3]. The details of the vehicle preconditioning, diurnal evaporative test, cold start exhaust test, and hot soak evaporative test are given in the Federal Register.[4]

Evaporative sources constitute, typically, 30 to 60 percent of the total hydrocarbon emissions from passenger gasoline vehicles with catalysts. The vapor pressure of most current Diesel fuels under ambient conditions is so low that Diesel evaporative emissions are very low. Diesel equipped vehicles are not currently subject to evaporative emission requirements.

FIGURE 1

EFFECT OF EMISSION CONTROL SYSTEM ON EXHAUST HYDROCARBON DISTRIBUTION



The evaporative emissions were found to be sensitive to the fuel composition and the vapor pressure of the fuel. All of the emitted hydrocarbons were greater than carbon number 4, normally the lowest molecular weight component of gasoline. A list of the test fuel specifications is given in Table 5. Four primary fuels were used. Fuels A and C were regular grade unleaded, summer and winter, respectively. Fuel B was a premium grade summer unleaded and Fuel D a regular grade winter leaded. Fuels A-1, B-1 and D-1 had increased benzene levels but did not differ in any other respect. These latter fuels were used to examine the sensitivity of fuel benzene content to benzene emissions. (These results and a complete analysis of benzene emissions from both Diesel and gasoline vehicles will be discussed in a later section.)

A summary of the results can be found in Table 6. Fuel C is the most similar in composition to the fuel used for comparison of catalyst, non-catalyst and lean-burn control systems in the previous section.

Evaporative sources constituted a significant fraction of the total vehicle aggregate hydrocarbon emissions, varying from about 1/3 to 1/2 with the vehicles tested. Evaporative emissions varied significantly with the Reid Vapor Pressure (RVP) of the fuel. As the RVP increases, the evaporative emissions also increase. Evaporative emissions, as mentioned before, are dominated by fuel hydrocarbon components. For this reason, they contain a greater abundance of low molecular weight paraffinic hydrocarbon compounds than do exhaust emissions. Increased aromatic content of the fuel caused increased aromatic content in both the tailpipe and evaporative emissions. High fuel vapor pressure generally resulted in increased paraffinic content of the emissions, resulting from the use of low molecular weight paraffins (butanes and pentanes) to increase fuel vapor pressure. As mentioned previously, evaporative emissions increase as the vapor pressure of the fuel increases. The trend in marketed gasolines during the last 30 years has been to increase vapor pressure. The relative proportion of evaporative hydrocarbon emissions has, therefore, also been increasing and should be considered when examining hydrocarbon emissions from gasoline vehicles.

TABLE 5

Test Fuel Specifications for Evaporative Emission Analysis

	FUEL CODES						
	A	A-1	B	B-1	C	D[1]	D-1
	Summer		Premium Summer		Winter	Winter	
RVP	8.4		9.8		12.3	12.8	
API Gravity	61.6		54.9		62.0	62.3	
Distillation, °F							
10%	133		126		114	108	
50%	207		219		219	217	
90%	285		327		362	347	
EP	376		369		410	418	
Hydrocarbon, Wt. %[2]							
n-butane	3.73		3.48		9.94	9.85	
i-pentane	6.94		11.19		7.85	8.15	
n-pentane	5.48		3.40		4.13	4.08	
benzene	0.28	7.1	1.52	7.1	1.95	1.83	5.8
toluene	17.55		27.91		6.30	6.01	
paraffinic	65.4		49.0		67.0	69.0	
olefinic	7.2		7.6		7.0	5.1	
aromatic	27.4		43.4		25.7	25.9	

1 leaded gasoline 1.98 g/gal.
2 analysis by gas chromatography

TABLE 6

Tailpipe and Evaporative HC Emissions

Vehicle	Fuel (RVP)	Tailpipe HC Composition % of Total						Evaporative HC Composition* % of Total					
		Paraffinic	Olefinic	Aromatic	Acetylenic	THC mg/mile	% of Total Aggregate THC	Paraffinic	Olefinic	Aromatic	THC mg/mile	% of Total Aggregate THC	Aggregate THC mg/mile
1963 Chevrolet	D (12.8)	42.0	27.1	20.7	10.2	4000	42	87.6	8.1	4.3	5600	58	9600
1977 Mustang	B (9.8)	43.2	16.0	40.7	0.2	2800	52	75.1	11.5	13.4	2600	48	5400
	C (12.3)	54.7	21.6	23.4	0.3	2800	44	82.4	11.4	6.1	3600	56	6400
1978 Monarch	A (3.4)	60.8	18.6	20.1	0.5	1000	83	80.1	8.7	11.2	200	17	1200
	B (9.8)	56.0	13.9	28.7	1.4	900	64	61.0	10.1	28.9	500	36	1400
	C (12.3)	63.7	18.6	14.2	3.5	1300	62	88.0	7.3	4.7	800	38	2100
1979 LTD-II	B (9.8)	58.3	10.9	29.9	0.9	500	63	57.1	8.1	34.8	300	37	800
	C (12.3)	72.8	11.6	11.0	4.6	500	17	89.9	7.7	2.4	2400	83	2900

*There is no acetylene in evaporative emissions.

$$EVAP = \frac{Di + 3.3 \text{ trips/day } (Hs)}{29.4 \text{ miles/day}}$$

Where:

EVAP = Total evaporative emissions, grams/mile.
Di = Diurnal evaporative emissions, grams/day.
Hs = Hot soak evaporative emissions, grams/trip.

III. Vehicles Equipped With Diesel Engines

Organics emitted from vehicles equipped with Diesel engines range from C_1 to about C_{40}, the majority being below C_{25}. The C_1-C_{10} hydrocarbons result almost entirely from the combustion process, which involves cracking, and possibly polymerization, of higher molecular weight materials. It is postulated that the C_{10}-C_{25} hydrocarbons result, to a large extent, from uncombusted fuel, and the C_{15}-C_{40} hydrocarbons from lubricants.

It is possible to identify the individual components of carbon numbers 1 through 10 with a gas chromatograph. The gas chromatograph used to measure the compounds with carbon numbers greater than 10 does not have adequate resolution to permit identification of each individual compound in this range. It is, however, possible to determine the molecular weight distribution of the compounds of interest. Since it is not currently possible to identify individual components of Diesel equipped vehicle exhaust, Diesel hydrocarbon analyses must be done in terms of carbon number.

The data used was taken from an EPA paper by F. Black[5]. The Diesel-equipped vehicles tested were prototypes, an Oldsmobile, a Nissan and a turbocharged Rabbit. The data was presented in terms of relative abundance of carbon number. We converted the data to units of milligram per mile for each carbon number. (These calculations can be found in the Appendix.) The fuel composition was 66.2% paraffin, 1.3% olefin and 32.5% aromatic. The 1975 Federal Test Procedure was used.

In the case of gasoline fueled vehicles, the hydrocarbon exhaust emissions are low molecular weight hydrocarbons and are virtually all in the gas phase at 125°F. These gaseous hydrocarbon emissions have routinely been measured with the total hydrocarbon flame ionization detector (FID) and exhaust samples collected in teflon film bags using a constant volume sampling (CVS) system. However, measurement of exhaust hydrocarbons from Diesel-equipped vehicles is much more difficult than with gasoline vehicles. This is due, in part, to the high molecular weight hydrocarbons present in Diesel exhaust. The teflon film bags used for gasoline vehicles cannot be used for the higher molecular weight gaseous hydrocarbons in Diesel exhaust because these heavy gaseous hydrocarbons are lost to the walls of the bags and other cool surfaces contacted on transport from the vehicle. The situation is further complicated by the fact that some of the hydrocarbons emitted from Diesels are associated with carbon particles, often referred to as particle-bound organics (PBO). The particle-bound organics are high molecular weight compounds. Diesel organic emissions, therefore, occur in two physical states, gaseous and particulate, and contain high molecular weight hydrocarbons.

A diagram of an experimental gaseous and particulate emissions sampling system for Diesel-equipped vehicles used in an EPA research project can be found in Figure 2[6]. The dilute exhaust is processed in two temperature regimes, at or below 52°C (125°F) and at 190°C (375°F). The measurement of total hydrocarbons is made in the hot sample stream. Heating

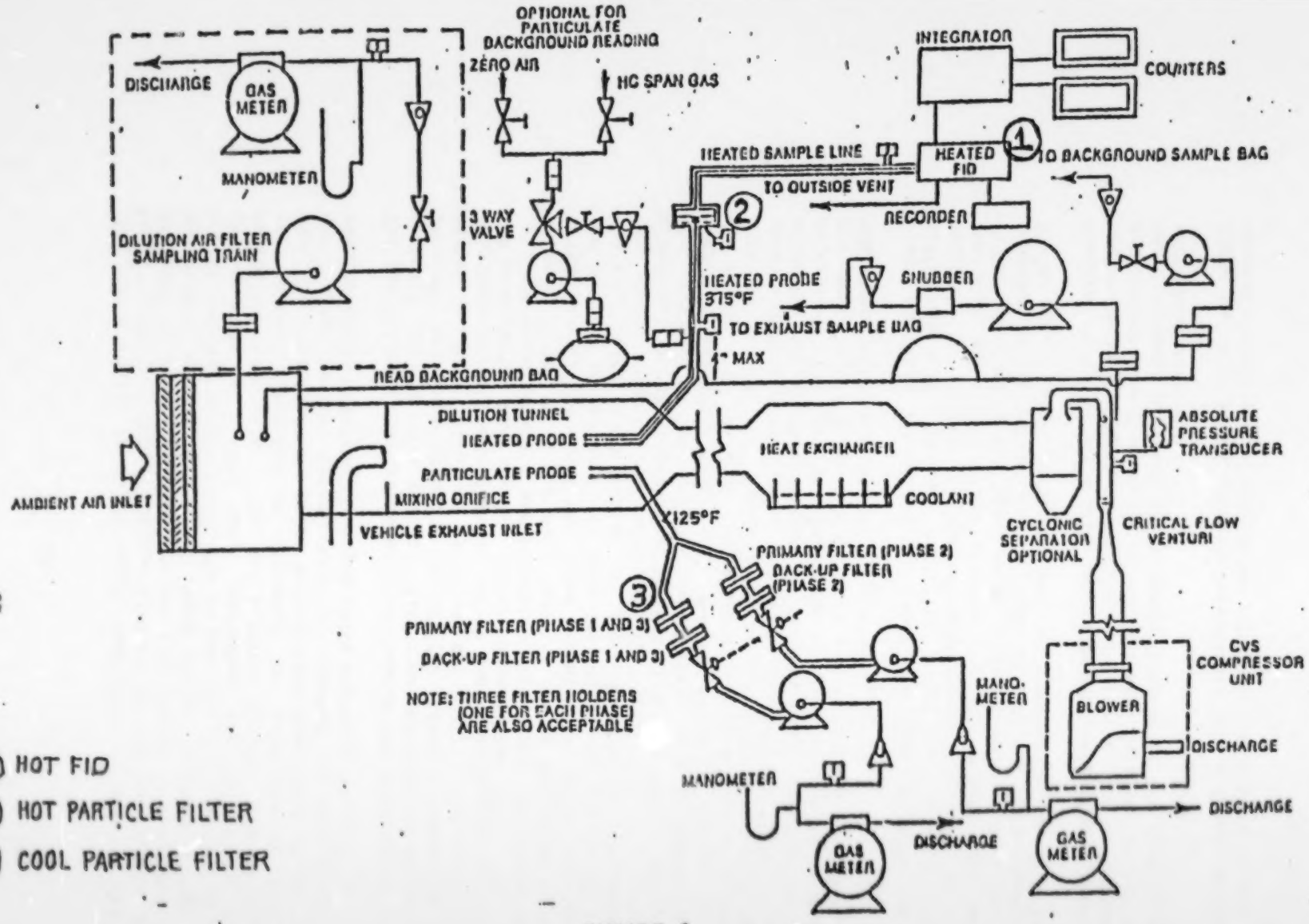


FIGURE 2
GASEOUS AND PARTICULATE EMISSIONS SAMPLING SYSTEM (CFV-CVS)
(FOR DIESEL VEHICLES ONLY)

the sample stream to 375°F causes desorption of most of the particle-bound organics. Any particles present in the hot sample stream are filtered at point (2), the hot particle filter, and solvent extracted. The gaseous element of the hot sample stream continues through point (2) and is detected at point (1), the heated FID. The quantity of hot filter extractables is a very small percentage compared to the hydrocarbon heated FID measurement. The cool particle filters, located at point (3), are solvent extracted to determine the emissions of particle-bound organics. The 125°F gas phase hydrocarbons downstream of the cool particle filter are the hydrocarbons of interest in this report and will hereinafter be referred to as gas phase organics (at 125°F).

The hot filter extractables plus the heated FID measurement are quantitatively compared with the cool filter extractables to obtain by difference the gas phase organics (at 125°F). Figure 3 summarizes the hydrocarbon analysis performed by Black and High[5]. The total hydrocarbon emissions in this experimental set-up can be considered to equal the hot FID measurement plus the hot filter extractables (HFE), A+C. The total particle-bound organics are determined by solvent extraction of the cool filters, D. The total gas phase organics can be determined by subtracting D from A + C. The total gas phase organics (at 125°F) are thus equal to the hot FID measurement (A) plus the hot filter extractables (C) minus the cool filter extractables (D) (hot FID+HFE-CFE). The measurement of gas phase organics is based on the assumption of conservation of organics, i.e. the organics in the hot filter stream are assumed to equal the organics in the parallel cool filter stream. Referring again to Figure 3, the total organics in the hot filter stream are equal to A+C. The organics in the cool filter stream are equal to D plus the gas phase organics (at 125°F). Equating the organic streams and isolating the gas phase organics gives: total gas phase organics (at 125°F) = A+C-D. The molecular weight distribution of the gas phase organics (at 125°F) are determined with gas chromatographic analysis of samples B, D and E. The gas phase organics (at 125°F) distribution is equal to B+E-D which gives the carbon distribution from C_{1-10} and C_{10-40}.

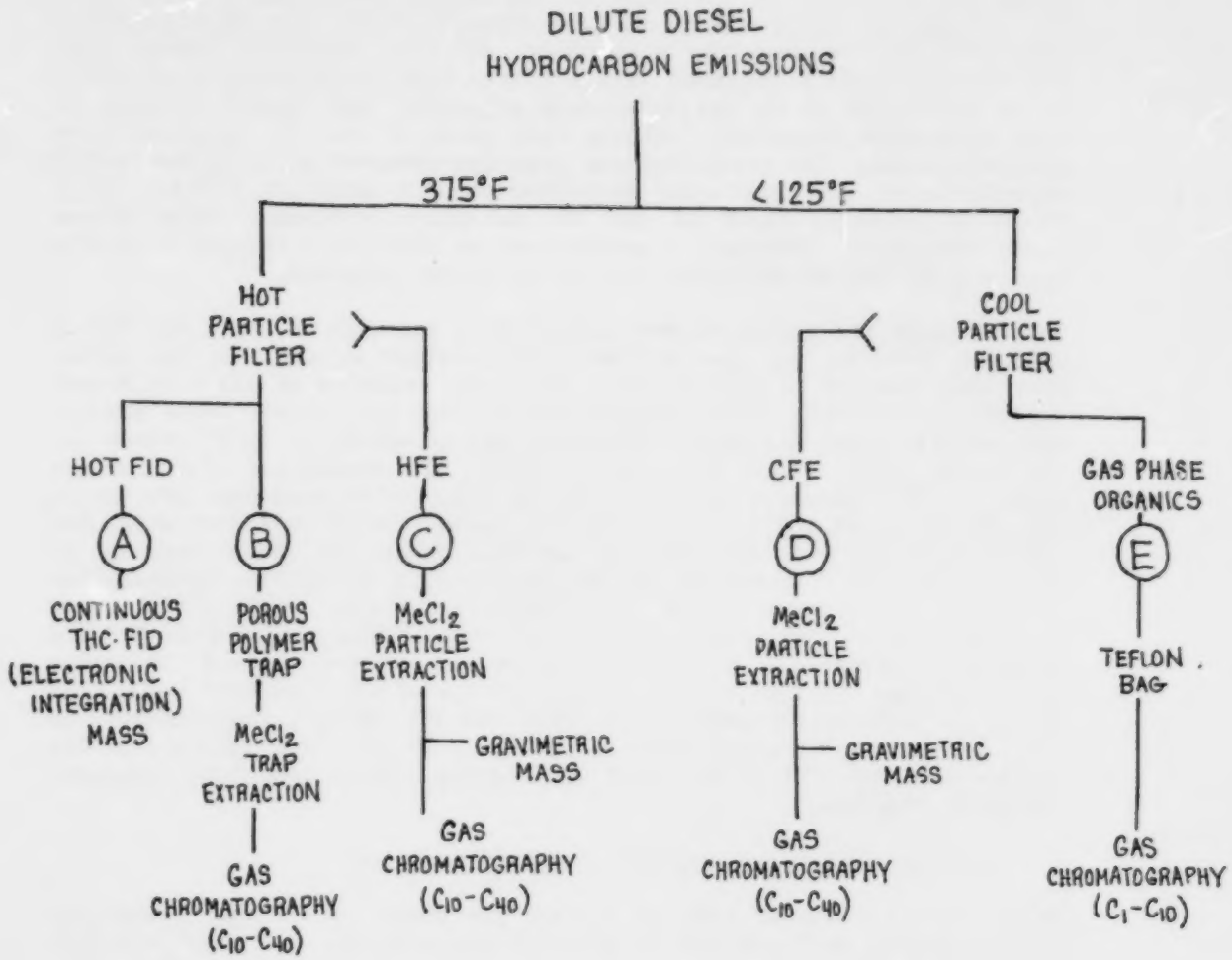
Black and High determined the total gas phase organics (at 125°F) by difference with the cool particles rather than using an FID directly behind a cool filter because of anticipated difficulty in transporting the high molecular weight gaseous organics through cool (at or below 125°F) plumbing which has a high ratio of surface area to volume. In contrast to the particle-bound organics, the gas phase organics (even at 125°F) from Diesel vehicles may be susceptible to wall interaction.

Research with multiple FIDs and alternate sampling systems has been performed in the past. Two FIDs were used during a light-duty Diesel particulate baseline study at the EPA/MVEL facility in Ann Arbor[7]. The two instrument approach is difficult because of the problem of variable instrument response.

Black and High have conducted experiments with a Nissan Diesel involving multiple tests with a single hot FID with and without a cold filter[8]. A

FIGURE 3

HYDROCARBON ANALYTICAL SCHEME



A: HOT FID = HEATED FLAME IONIZATION DETECTOR

C: HFE = HOT FILTER EXTRACTABLES

D: CFE = COOL FILTER EXTRACTABLES

E: GAS PHASE ORGANICS = A + C − D

standard hot FID system was used to measure THC followed by determination of THC emissions with the same hot FID but with a pallflex (teflon coated glass fiber) filter on the inlet to the sample probe inside the tunnel. The average of three FTP tests were determined for each configuration. The difference between the measurement obtained without a filter (THC) and the measurement obtained with a filter (gas phase organics at 125°F) is an indication of the particle-bound organics. The results obtained by this difference procedure indicate that 16.1% of the THC emissions were particle-bound. The particle-bound organics measured by methylene chloride extraction of the particles collected on the pallflex filters (26°C or 79°F) indicate 16.6% of the THC was particle-bound. These values agree very well. However, a system such as this would require duplicate runs and may not be practical for certification purposes.

Table 7 lists the carbon number distribution for each of the three Diesel equipped vehicles and also includes the averaged values from the three. From this data it is evident that gas phase organics at 125°F in Diesel exhaust have a wide carbon number distribution and contain small quantities of high molecular weight organics. Approximately 60 to 85 percent of the total hydrocarbons in Diesel exhaust are associated with the gas phase at 125°F which means 15-40% of the hydrocarbon compounds are not in the gas phase at 125°F. (We would once again like to emphasize that, for the Diesel-equipped vehicles, we are discussing gas phase organics at 125°F, i.e. the measurement of heated FID plus hot filter extractables less cool filter extractables. Gas phase organics in Diesel exhaust are, for the sake of this paper, considered to be those organics in the gas phase at or below 125°F.) The Diesel equipped Rabbit emitted the lowest mass, followed by the Oldsmobile and the Nissan which emitted more. The emissions were approximately 244, 273, and 295 mg/mile respectively, as measured by the aforementioned procedure. To put this data in proper perspective, it will be compared with carbon number data from catalyst-equipped vehicles.

IV. Diesel-Equipped vs. Catalyst-Equipped Vehicles

Tables 3 and 7 can be used to compare gas phase carbon number data for the light-duty gasoline and Diesel-equipped vehicles. It should be kept in mind that 13 vehicles equipped with catalysts were used in this analysis in contrast to only 3 vehicles equipped with Diesel engines. Neither the prototype Diesel equipped vehicles nor the catalyst-equipped gasoline vehicles were designed to meet the 1980 0.41 g/mile total hydrocarbon emissions standard. Unfortunately, the available information is limited to older vehicles. The data presented may not be representative of more recent production models; however, it is likely reflective of current on-roadway conditions.

Based on average values, the Diesel-equipped vehicles have higher molecular weight gaseous organics but emit lower emissions (approximately 270 mg/mile for the Diesels, 450 mg/mile for the catalyst-equipped vehicles). The higher hydrocarbon mass for the catalyst-equipped vehicles is partially attributable to a greater percentage and mass of methane in the catalyst exhaust (14.3% methane in the catalyst exhaust compared to 6.5% in the Diesel exhaust).

TABLE 7

Carbon Number Data for Diesel-Equipped Vehicles

Carbon Number	Weight of Gas Phase Component, mg/mile			
	Olds Diesel	Nissan Diesel	Turbo-Charged Rabbit Diesel	Average
1	22	21	12	18
2	72	60	60	64
3	18	16	16	17
4	14	14	11	13
5	10	7	6	8
6	16	14	11	14
7	7	14	7	9
8	7	4	—	5
9	4	3	—	4
10	5	24	4	11
11	6	22	6	11
12	7	10	5	7
13	10	12	10	11
14	14	19	10	14
15	15	13	14	14
16	13	10	11	11
17	9	10	11	10
18	5	6	9	7
19	4	5	7	5
20	3	2	4	3
21	2	2	4	2
22	2	2	3	2
23	2	.5	3	2
24	.5	1	3	2
25	1	1	3	2
26	.5	.1	4	1
27	.5	—	2	1
28	.5	—	3	.4
29	.5	.5	.3	.4
30	.5	.5	2	1
31	1	1	.7	.9
32	.5	1	1	.9
33	.1	1	1	.7
34	.2	1	1	.7
35	.5	.5	.5	.4
36	.2	.5	1	.6
37	.2	—	.5	.4
38	.5	—	—	.5
39	1	—	—	1
40	.2	—	—	.2
41	.5	—	—	.5
42	.2	—	—	.2
43	.1	—	—	.1
Total	275	295	244	277

Diesel engine exhaust, including gas phase organics and particle-bound organics tends to be heavier than gasoline-catalyst exhaust. This is due mainly to the hydrocarbon fraction with carbon numbers C_{10} - C_{25}. These tend to contain a high percentage of aromatics which are of concern as some members of this class of compound have been found to give positive results in initial bioassay screening tests for carcinogenicity. To date, samples examined for mutagenicity/carcinogenicity have consisted of organics extracted from particulate material. Methods for collection of the gas phase organics are not sufficiently developed at this time to allow direct bioassay testing of gaseous material. Nevertheless, the presence of these heavier, higher molecular weight compounds in Diesel exhaust cannot be overlooked as these compounds have not all been identified and may pose health risks.

Figure 4 compares gaseous hydrocarbon emissions by carbon number for a gasoline fueled VW Rabbit with an oxidation catalyst[1] and a prototype turbocharged VW Rabbit equipped with a Diesel engine. Data for the Diesel-equipped Rabbit can be found in Table 7, for the catalyst-equipped Rabbit in Table 8. Figure 4 provides a direct and easier comparison for each carbon number. The VW gasoline Rabbit emitted 180 mg/mile in comparison to 240 mg/mile for the Diesel-equipped Rabbit. In this case, the Diesel gaseous emissions were approximately 33% higher. The Diesel emitted more gaseous compounds of carbon numbers 2, 3, 6, and 10 or greater. The gasoline Rabbit emitted more compounds of carbon numbers 1 (methane), 4, 5, 7, 8, and 9. The Diesel-equipped vehicle consistently emits a greater percentage of heavier, unidentified hydrocarbons in its exhaust. As mentioned previously, this is significant as one or more of these compounds may be carcinogenic.

V. Carcinogenicity - Benzene Emissions

Benzene has been determined to be a hazardous pollutant and a potential carcinogen. Benzene is present in both gasoline and Diesel exhaust and, in addition, in gasoline evaporative emissions. Because of benzene's association with cancer, it is of importance to examine the emission rates of benzene from gasoline and Diesel-equipped vehicles.

Table 9 presents benzene data from one non-catalyst and three catalyst-equipped vehicles. Both tailpipe and evaporative benzene emission rates are included. These are the same vehicles and fuels used for the evaporative emission analysis. (When comparing fuels it should be noted that typical commercial gasoline benzene content is less than 2 percent. Diesel fuel contains insignificant levels of benzene.)

Benzene emissions reflected both fuel benzene and fuel total aromatic content. The fuel benzene level had a more pronounced impact on evaporative emission rates than tailpipe rates. This is expected because the fuel is the only source of benzene in evaporative emissions whereas the combustion process is a significant additional source in tailpipe emissions. Under normal operating conditions evaporative benzene accounted for 20 to 30% of the total aggregate benzene emissions. Both tailpipe and evaporative

TABLE 8

Carbon Number Data for the Catalyst-Equipped VW Rabbit

Carbon Number	Weight, mg/mile	Compounds
1	34	methane
2	18	ethylene, ethane, acetylene
3	5	propylene, propane
4	12	isobutane, butene-1, isobutylene n-butene, 1,3-butadiene, cis-2-butene
5	34	isopentane, pentene-1, n-pentane, 2-methyl-1-butene, trans-2-pentene, cis-2-pentene, 2-methyl-2-butene, cyclopentane
6	8	2,3-dimethylbutane, 2-methylpentane, 2,3-dimethyl-1-butene, 3-methylpentane, 1-hexene, 2-ethyl-1-butene, n-hexane, cis-3-hexene, 2-methyl-2-pentene, methylcyclopentane, 3-methtrans-2-pentene, 3-methyl-1-pentene, cyclohexene, benzene, cyclohexane
7	29	2,4-dimethylpentane, 3-methylhexane, n-heptane, methylcyclohexane, 2,3-dimethylpentane, 2-methylhexane, toluene
8	29	isooctane, 2,3-, 2,4- and 2,5-dimethylhexane, 2,3,4-trimethylpentane, 2- and 3-methylheptane, n-octane, ethylbenzene, p-, o- and m-xylene
9	7	2, 2, 5-trimethylhexane, 2,3-, 2,4-, 2,5- and 3,5-dimethylheptane, nonane, n-propylbenzene, 4-methyloctane, unknown C_9 paraffin, 1-methyl-3-ethylbenzene
10	0.6	secbutylbenzene, n-decane, unknown C_{10} paraffin
Unknowns	5	
Total	180	

FIGURE 4

Comparative Emissions of Gas Phase Hydrocarbons from Two VW Rabbits

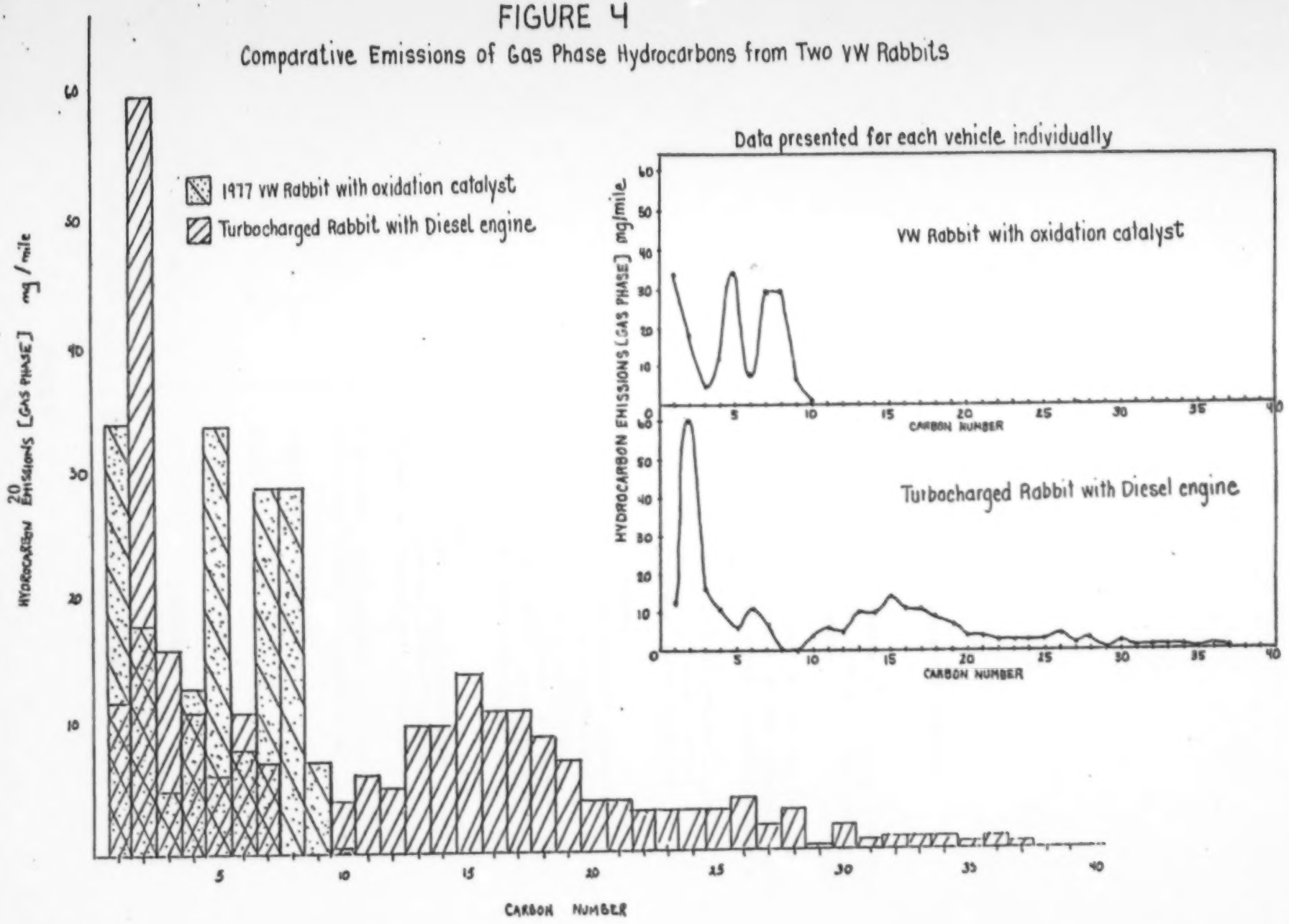

1977 VW Rabbit with oxidation catalyst
Turbocharged Rabbit with Diesel engine
HYDROCARBON EMISSIONS [GAS PHASE] mg/mile
CARBON NUMBER
Data presented for each vehicle individually
VW Rabbit with oxidation catalyst
Turbocharged Rabbit with Diesel engine
HYDROCARBON EMISSIONS [GAS PHASE] mg/mile
CARBON NUMBER

Table 9 Passenger Car Benzene Emissions

Vehicle	Code	Fuel Aromatic,%	Benzene,%	Tailpipe Benzene Mg/mi	% of aggregate	Evaporative Benzene Mg/mi	% of aggregate	Aggregate Mg/mi
1963	D	25.9	1.8	153	82	33	18	186
Chevrolet	D-1	28.9	5.8	327	63	192	37	519
1977	B	43.4	1.5	292	86	48	14	340
Mustang	B-1	46.6	7.1	397	73	146	27	543
	C	25.7	2.0	190	77	58	23	248
	A	27.4	0.3	30	97	1	3	31
1978	A-1	32.4	7.1	58	84	11	16	69
Monarch	B	43.4	1.5	30	77	9	23	39
	C	25.7	2.0	33	87	5	13	38
	B	43.4	1.5	25	78	7	22	32
1979	B-1	46.6	7.1	35	62	21	38	56
LTD-II	C	25.7	2.0	14	54	12	46	26

benzene increased with increasing benzene content of fuel. Fuel aromatic % also influenced both tailpipe and evaporative benzene. Tailpipe benzene rates were higher with the higher aromatic fuels. There was also an increase in benzene in tailpipe emissions under rich combustion conditions.

Table 10 presents a general summary of benzene tailpipe emissions from catalyst and Diesel-equipped vehicles. Data for the catalyst-equipped vehicles was based on 15 vehicles while only 8 vehicles were tested for the Diesel analysis.

Benzene and cyclohexane peak at the same point on the gas chromatograph. The percentage each compound contributes to this peak for the catalyst-equipped vehicles is dependent on the fuel used. In this case,for the catalyst-equipped vehicles, the peak is composed of approximately 50% benzene and 50% cyclohexane. The benzene data for the Diesel-equipped Oldsmobile, Nissan and Turbo-Rabbit was presented as a percentage of the total hydrocarbon measurement (for these vehicles total hydrocarbons can be considered to equal the hot FID measurement plus the hot filter extractables). Benzene constitutes one of the gas phase organics in Diesel exhaust. Benzene has not been found bound to particulate matter.

The highest emitter of tailpipe benzene was the 1978 gasoline Monarch with an emission rate of 33 mg/mile. Evaporative benzene can account for up to 20 to 30% of the total aggregate benzene from gasoline vehicles and is an additional factor that should be kept in mind when examining gasoline benzene emissions. Unfortunately, there was not enough data to include this type of information here. The catalyst-equipped vehicles emitted from 1.1 to 2.8 percent of their tailpipe hydrocarbons as benzene.

The Diesel data were similarly scattered; the Diesels emitting 0 to 3.8 percent of their tailpipe hydrocarbons as benzene. The Mercedes 220D Comprex emitted a low mass of benzene and total hydrocarbons, yet had the greatest percentage of benzene in its hydrocarbon exhaust (3.8%). In contrast, the Mercedes 240D and the Peugeot 204D had no benzene in the exhaust. As a rough comparison, tailpipe benzene emission rates vary from 0 to 15.4 mg/mile for the Diesel-equipped vehicles and from 2.4 to 33 mg/mile for the catalyst-equipped vehicles, based on this data.

Summary

1. Gas phase hydrocarbon emissions from light-duty gasoline and Diesel-equipped vehicles were examined and compared. The hydrocarbon composition of gasoline exhaust consists primarily of components of carbon numbers 1 through 10. In contrast, the gas phase organics from vehicles equipped with Diesel engines range from C_1 to about C_{40}, and contain small quantities of high molecular weight organics.

2. The hydrocarbon data presented for the Diesel-equipped vehicles were limited to three vehicles. In contrast, individual hydrocarbon data for 13 catalyst-equipped vehicles were available. The catalyst-equipped vehicles were well tuned and thus may not always represent in-use vehicles. These factors should be taken into consideration when evaluating the results.

TABLE 10

PASSENGER CAR BENZENE EMISSIONS FOR CATALYST-EQUIPPED AND DIESEL-EQUIPPED VEHICLES

Vehicle	Fuel % Aromatics	Tailpipe Benzene mg/mile	Tailpipe THC mg/mile	% Benzene
Catalyst				
Average of[1] 13 vehicles	26.2	5.1 Min. 2.4 Max. 11.8	450 Min. 180 Max. 920	1.1 Min. 1.3 Max. 1.3
From Table 2				
1978 Monarch[3]	25.7	33	1300	2.5
1979 LTD II[3]	25.7	14	500	2.8
Diesel				
Oldsmobile[5]	32.5	13.4	450	3.0
Nissan[5]	32.5	9.4	350	2.7
Turbo-Rabbit[5]	32.5	2.4	290	.83
Mercedes 220D[9]	25.6	9.8	260	3.8
Mercedes 240D[9]	25.6	0.0	210	0.0
Mercedes 300D[9]	25.6	4.0	160	2.5
Peugeot 204D[9]	25.6	0.0	1600	0.0
Perkins 6-247[9]	25.6	15.4	720	2.1

NOTE: The numbers 1, 3, 5, and 9 refer to the numbered references given at the end of this paper.

THC values for the Diesel-equipped Oldsmobile, Nissan and Turbo-Rabbit include both hot FID and hot filter extractables.

The 1975 FTP was used for every vehicle.

3. The catalyst tends to oxidize the unsaturated hydrocarbon compounds to a greater extent than the saturated compounds. Methane is a saturated compound and, because of its refractory nature, is the least oxidized compound. This explains the high percentage of methane in exhaust from vehicles equipped with catalysts. The Diesel, in turn, appears to have a greater percentage of unsaturated hydrocarbons such as olefins and aromatics in its exhaust.

4. Further detailed hydrocarbon comparisons are hampered by the lack of data on higher molecular weight organics in the exhaust from Diesel-equipped vehicles. One or more of these unidentified high molecular weight organics may be carcinogenic.

5. Available data indicated that exhaust gaseous benzene emissions from gasoline catalyst-equipped and Diesel-equipped vehicles are roughly equivalent. Additional evaporative emissions of benzene (which occur from gasoline vehicles but not Diesel-equipped vehicles) may be as high as 50% of the exhaust emissions based on limited tests run to date.

6. The collection of data on individual components of exhaust and evaporative emissions is significant in that individual carcinogenic potency can be examined. Identification of emissions by structure or class of compound is useful but ignores individual potency that may be important.

7. Some of the hydrocarbons in Diesel-equipped vehicle exhaust are of high molecular weight. These heavy exhaust hydrocarbons are found both in the gas phase and bound to particulate matter. While extensive Ames bioassay testing for mutagenicity is being performed on the organics extracted from the particulate, the relative mutagenicity of the gas phase organics remains unknown. To date, no method exists to collect gas phase hydrocarbons in exhaust for bioassay testing although work is in progress to develop such a method.

References

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4. Federal Register, "Final Evaporative Emission Regulations for Light-Duty Vehicles and Trucks", Vol. 41, No. 164 (August 23, 1976).

5. F. Black and L. High, "Methodology for Determining Particulate and Gaseous Diesel Hydrocarbon Emissions", SAE 790422.

6. Federal Register, "Standard for Emission of Particulate Regulation for Diesel-fueled Light-Duty Vehicles and Light-Duty Trucks", Vol, 45, No. 45 (March 5, 1980).

7. Private communication with Eugene Danielson, EPA, Ann Arbor, Michigan July 1980. Data contained in Technical Support Report SDSB 79-03, "Particulate Measurement-Light-Duty Diesel Particulate Baseline Test Results", January 1979.

8. F. Black and L. High, "Diesel Hydrocarbon Emissions, Particulate and Gas Phase", presented at the Symposium on Diesel Particulate Emissions Measurement and Characterization, May 17-18, 1978, Ann Arbor, Michigan.

9. K. Springer and R. Stahman, "Diesel Car Emissions - Emphasis on Particulate and Sulfates", SAE 770254.

Appendix

The carbon number data for the Diesel-equipped vehicles was given in terms of relative abundance. The heated FID, cool filter extractable and hot filter extractable emission rates were given in units of g/mile[6]. Table A-1 lists the relative abundances for each carbon number. Once the relative abundances were available for each carbon number for the hydrocarbons of interest, the carbon number data was converted to emission rates in units of mg/mile (see Table A-2). In this way, the data was in a form that could be directly compared to data from gasoline catalyst-equipped vehicles. The method of calculation is included in this appendix. All figures in the Appendix and in Tables A-1 and A-2 come from reference 6.

TABLE A-1

RELATIVE ABUNDANCE DATA

C#	OLDS relative abundance [ht, cm]		NISSAN relative abundance [ht, cm]		TURBO-CHARGED RABBIT relative abundance [ht, cm]	
	GP	Particulate	GP	Particulate	GP	Particulate
1	2.1	—	2.1	—	1.2	—
2	6.88	—	5.9	—	5.78	—
3	1.75	—	1.55	—	1.35	—
4	1.35	—	1.4	—	1.05	—
5	.95	—	.7	—	.55	—
6	1.55	—	1.35	—	1.1	—
7	.65	—	1.35	—	0.7	—
8	.65	—	.4	—	—	—
9	.4	—	.3	—	—	—
10	.5	—	2.4	—	.4	—
11	.6	—	2.2	—	.35	—
12	.65	—	.95	.03	.45	—
13	1.0	—	1.2	.03	1.0	—
14	1.3	.05	1.85	.05	1.0	—
15	1.45	.15	1.25	.07	1.35	.03
16	1.25	.25	.95	0.1	1.05	.05
17	.85	.35	.95	.15	1.05	0.1
18	.5	.6	.55	.2	.85	.2
19	.35	.75	.45	.35	.65	.35
20	.25	.8	.2	.5	.4	.45
21	.15	.6	.2	.6	.35	.5
22	.15	.45	.15	.5	.??	.45
23	.15	.4	.05	.45	.25	.4
24	.05	.45	.1	.35	.3	.35
25	.1	.5	.1	.25	.3	.35
26	.05	.65	.01	.25	.35	.35
27	.05	.75	—	.25	.15	.25
28	.05	.85	—	.2	.25	.3
29	.05	.95	.05	.15	.03	.2
30	.05	1.0	.05	.15	.2	.15
31	.1	1.0	.1	.1	.07	.1
32	.05	1.0	.1	.1	.1	.15
33	.01	.85	.1	.1	.1	.05
34	.02	.9	.1	.1	.1	.05
35	.05	.9	.05	.1	.05	.03
36	.02	.85	.05	.1	.12	—
37	.02	.8	—	.07	.05	—
38	.05	.6	—	.03	—	.02
39	.1	.45	—	.02	—	.02
40	.02	.35	—	.02	—	.02
41	.05	.25	—	—	—	—
42	.02	.2	—	—	—	—
43	.01	.15	—	—	—	—
44	—	.1	—	—	—	—
45	—	.02	—	—	—	—
TOTAL	26.35	17.97	29.64	7.62	23.7	4.92
Conversion	10.4		10.1		10.3	

from F. Black & L. High SAE 790422

TABLE A-2

RELATIVE ABUNDANCE CONVERSIONS AND CALCULATIONS

	OLDS	NISSAN	RABBIT
A. Given Values (mg/mile)			
HFE = hot filter extractables	11	8	3
HOT FID = heated flame ionization detector	445	349	292
CFE = cool filter extractables	181	58	50
(Hot FID + HFE - CFE) = diesel hydrocarbon measurement of interest	275	299	245
B. Calculated Values (mg/mile)			
$GPn = \left[\frac{RAn}{RAg}\right] \times$ (Hot FID + HFE - CFE)	(Hot FID + HFE - CFE) =275 mg/mile	(Hot FID + HFE - CFE) =299 mg/mile	(Hot FID + HFE - CFE) =245 mg/mile
where:	RAg=26.35	RAg=29.66	RAg=23.7
GPn = weight of (Hot FID + HFE - CFE) hydrocarbons of carbon number n, mg/mile	$\therefore$ GPn=10.4 (RAn)	$\therefore$ GPn=10.1 (RAn)	$\therefore$ GPn=10.3 (RAn)
RAn = relative abundance of (Hot FID + HFE - CFE) component of carbon number n			
RAg = total relative abundance of (Hot FID + HFE - CFE) component			
C. Sample Calculation For C=10			
	GP_{10}=10.4 (RA_{10})	GP_{10}=10.1 (RA_{10})	GP_{10}=10.3 (RA_{10})
$GP_{10} = \left[\frac{RA_{10}}{RAg}\right] \times$ (Hot FID + HFE - CFE)	RA_{10}= 0.5	RA_{10} = 2.4	RA_{10} = 0.4
	$\therefore GP_{10}$=5 mg/mile	$\therefore GP_{10}$=24 mg/mile	$\therefore GP_{10}$=4 mg/mile
(These numbers can be compared with those in Table 7.)			